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Sensitized extraction spectrophotometric determination of Hg(II) with dithizone after its flotation as ion-associate using iodide and ferroin

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Abstract

This paper describes a simple and highly selective method for the separation, preconcentration and spectrophotometric determination of extremely low concentration of mercury. The method is based on the flotation of an ion-associate of HgI_4^{2-} and ferroin between aqueous and *n*-heptane interface at pH 5. The ion-associate was then separated and treated with ammonia and dithizone solutions to extract only the mercury chelate with CH_2Cl_2. The measurement is feasible when the volume of the water sample containing Hg(II) was varied over 50–800 ml. Beer's law was obeyed over the concentration range of 8×10^{-9} to 1.6×10^{-7} mol l^{-1} with an apparent molar absorptivity of 6.53×10^{6} l mol^{-1} cm^{-1} for a 500 ml aliquot of the water sample. The detection limit ($n = 7$) was 5.0×10^{-10} mol l^{-1} and the R.S.D. ($n = 5$) for 8.0×10^{-7} mol l^{-1} of Hg(II) was 3.7%. A notable advantage of the method is that the determination of Hg(II) is free from the interference of almost all cations and anions found in the environmental and waste water samples. The determination of Hg(II) in tap, synthetic sea water and human hair samples was carried out by the present method and cold vapor atomic absorption spectrometry (CV-AAS). The results were satisfactorily comparable so that the applicability of the proposed method was confirmed to the real samples.

Keywords: Flotation–extraction; Mercury determination; Dithizone; Spectrophotometry

1. Introduction

Inorganic and organic mercury compounds are widely distributed on the earth and can be exposed easily to the human environment [1]. Thus, monitoring the environment in view of mercury pollution is very important. Generally, the concentration of Hg(II) in the environmental samples is very low unless exposed in some industrial area. The development of analytical methods for the determination of extremely low concentration of Hg(II) is still a challenge. Consequently, considerable effort and progress have been made to develop the techniques in which the determination of Hg(II) in the contaminated samples is carried out rapidly without any complicated processing steps. Most common techniques that have been reported for the determination of total mercury in natural samples are inductively coupled plasma mass spectrometry (ICP-MS) [2], inductively coupled plasma atomic emission spectrometry (ICP-AES) [3,4], gas chromatography (GC) coupled to atomic absorption spectrometry (AAS) [5–7], cold vapor atomic absorption spectrometry (CV-AAS) [8–11], atomic fluorescence spectrometry (AFS) [12], anodic stripping voltammetry (ASV) [13,14], neutron activation analysis (NAA) [15] and so on. Among these techniques, ICP-AES and ICP-MS are useful in determining the ultra trace of total mercury without any preconcentration step. However, these instruments are very expensive and costly for the maintenance. CV-AAS has been widely used with the considerable merits such as high sensitivity and little interference effect but this method suffers

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somewhat from poor precision and accuracy. In some techniques, separation and preconcentration via methods such as liquid–liquid extraction, ion-exchange, co-precipitation, should be performed to determine extremely low concentration of mercury [16]. However, these procedures are tedious and usually suffer from not reliable data in some cases. These drawbacks may be partly avoided using a technique that enables to separate and preconcentrate ultratrace amounts of Hg(II) in the various samples. Among the most useful methods, flotation techniques are of benefit to trace the elemental determination [17]. The advantages of adsorptive flotation technique for removing interfering components from the test solutions and for preconcentration of some metal ions are well-known [18–28]. Recently, the determination of mercury in some complex matrix was extended to a limit of 3.2×10^{-8} mol l^{-1} by this method [29]. Despite of the high capability of the flotation process, due to the insufficient sensitivity of ferroin as a dye reagent, determination of the lower concentration is not feasible with the above method. Thus, to increase the sensitivity and handling the determination with a lower detection limit, a better reagent should be employed.

One of the means to achieve a favorable sensitivity is utilizing the flotation process coupled with an extraction procedure and carrying out the determination in the presence of a dye reagent [30–33].

This paper deals with a rapid procedure for extraction-spectrophotometric determination of Hg(II) with dithizone following its flotation as an ion-association complex with iodide and ferroin.

2. Experimental

2.1. Materials and instrumentation

All the reagents were of analytical grade obtained from Merck, Germany. Double distilled fresh water was used in all the experiments. The standard solution of 1.6×10^{-3} mol l^{-1} Hg(II) was prepared by dissolving the appropriate amount of $Hg(NO_3)_2$, H_2O in 0.14 mol l^{-1} HNO_3. The required volumes of this solution were used to prepare the working solutions. An acetic–acetate buffer solution with the concentration of 0.1 mol l^{-1} was prepared by mixing nearly the appropriate amounts and adjusting to pH 5 by the addition of a few drops of HCl/NaOH solutions. The solution of 6.25×10^{-3} mol l^{-1} ferroin was made by sequential stoichiometrically dissolving of 1,10-phenanthroline (phen) and $FeSO_4$ in the appropriate amount of fresh water and adjusting the pH to 5 by the addition of diluted acetate buffer solution. The pure stable dithizone solution (1×10^{-3} mol l^{-1}) was prepared by dissolving the appropriate amount in CH_2Cl_2 (50 ml). This solution was filtrated through a sintered glass filter and shaken in a separating funnel with three 10 ml portions of 1% ammonia, to leave the oxidation products and any traces of metal dithizonates in the CH_2Cl_2 solution. The ammoniacal solutions containing dithizone as the ammonium salt were combined and washed with three 10 ml portions of carbon tetrachloride solvent, to assure from elimination of all the impurities, which may remain afterward the processing. By the addition of diluted hydrochloric acid to acidify the ammoniacal solution, the purified dithizone content was precipitated which was then extracted with carbon tetrachloride solvent. This organic solution was diluted to the mark and standardized by the extractive titration method with a standard silver solution [34]. A working solution with the concentration of 1.6×10^{-4} mol l^{-1} was made from the above standard solution which was kept cooled in a brown stoppered bottle during its storage.

A Shimadzu model 160 A spectrophotometer was used for all the absorbance measurements with a 10 mm quartz cell. A Shimadzu model 6300 atomic absorption spectrophotometer was used for cold vapor measurement technique. A Corning model 125 pH meter was used for pH measurements.

2.2. Procedure

To a 500 ml portion of a solution containing up to 16 μg Hg^{2+}, 5 ml 0.12 mol l^{-1} potassium iodide was added and its pH was adjusted to 5 by the addition of the buffer solution. The solution was transferred to a 1000 ml separating funnel, and then 2.5 ml ferroin and 40 ml *n*-heptane were added, sequentially. The funnel was stoppered and vigorously shaken for 10 min, and then left to rest for a few minutes to give a perfect floated layer in the aqueous/organic interface. By slowly opening the stopcock of the funnel, both the organic and aqueous layers were released (the organic layer was repetitiously used without any purification) whereas the floated layer was adsorbed on the inner walls of the funnel. To extract the mercury content, 50 ml 2.5% ammonia and 5 ml 1.6×10^{-4} mol l^{-1} dithizone solutions were added to the funnel and vigorously shaken again for 5 min. The organic phase containing just the mercury–dithizonate chelate was separated and its absorbance was measured at 490 nm against a reagent blank prepared in the same manner.

3. Results and discussion

3.1. Justification

As pointed above, the procedure includes two steps. Initially, separation and preconcentration of Hg(II) were carried out by its flotation as an ion-associate with iodide and phen, and then the determination was accomplished through the extraction-spectrophotometric method with dithizone. To obtain reliable results, a number of parameters influencing the steps were optimized. Some of them that related to the flotation step including the type of the organic layer, pH of the solution, concentration of iodide and phen, were firstly investigated and reported in our previous work [29]. The others that related to the extraction and determination of Hg(II) content are discussed as the following. Since almost all the interfering agents were eliminated via the flotation process, there is not so much troublesome on the performance of the extraction procedure. However, there is an inherent interference, due to the presence of iodide and Fe(II), which can not be eliminated even by properly proceeding the initial step. In this viewpoint, selection of a suitable reagent to extract the Hg(II) content gives emphasis on the following considerations.

1. Due to the high stability constant of HgI_4^{2-} complex, the reagent should form a much more stable complex with Hg(II).
2. In viewpoint to increase the sensitivity of the determination, the molar absorptivity coefficient of the extracted complex must be inherently much greater than the ion-associate which is in turn justifying the extraction step, evidently.
3. Subsequent to the flotation step, Fe(II) and phen are essentially present in the medium. Thus, the extraction process of Hg(II) should be carried out using a reagent with a high selectivity to avoid any interfering element in the extraction process.
4. To assure on quantitative extraction of Hg(II) content in one step, the gain of the extraction process must be very high.

In order to find a favorable reagent for the extraction process, a number of conventional reagents were investigated. It was observed that some of them, such as 2-mercaptobenzothiazole, mercaptobenzimidazole, diethyldithiocarbamate, were not able to extract Hg(II) completely in the presence of iodide. In treatment with 4-(3-thiazoleazo) resorsinol (TAR) and some analogous compounds, the Fe(II) ions were extracted simultaneously with Hg(II).

Dithizone is one of the foremost extractant, which is recognized as a sensitive reagent for the determination of Hg(II), both in acidic and basic media. It is capable to form primary and secondary dithizonates with Hg(II) in acidic and alkaline media, respectively [34,35]. However, due to a higher absorptivity coefficient and solubility in the organic phase, the primary mercury–dithizonate chelate was preferred in the spectrophotometric determination. Generally, to enhance the selectivity of the extraction of the primary mercury-dithizonate, the process is carried out in acidic medium in the presence of excess dithizone. It was seen, however, that a high excess amount of dithizone was co-extracted with the primary form. The co-existence of the reagent with its mercury chelate in the organic phase gave rise to serious spectral interference which prevented the proper determination of ultra trace amount of Hg(II). To overcome this problem, the extraction was carried out in a weak basic medium according to the mono-color method [36]. That is, after the flotation process and removing both the aqueous and organic phases, an aliquot of the ammonia solution was added to the funnel which is capable to neither dissolve nor decompose the ion-associate, but upon addition of the organic dithizone solution, the ion-associate was completely decomposed and only the primary mercury chelate was extracted with the organic phase. It must be pointed out that both the dissociation of the ion-associate and the formation of the primary mercury complex takes place just at the interface of the aqueous/organic layer. Thus, the ammoniacal solution is characterized as an acceptor phase to dissolve the excess amount of dithizone together with the residual components of the dissociate.

3.2. Optimization

It was very important to use dithizone with a sufficient high concentration to extract all the Hg(II) content in one step. The effect of dithizone concentration was studied over the concentration range of 1×10^{-5} to 2×10^{-4} mol l^{-1}. As shown in Fig. 1, maximum absorbance occurs to dithizone concentrations above 8×10^{-5} mol l^{-1}. Since by increasing the concentration of Hg(II) ions, a greater amount of dithizone was required, a solution with 1.2×10^{-4} mol l^{-1} dithizone was chosen for further investigations.

The ammonia concentration and its volume also influences the extraction process. With regard to the concentration of ammonia which is used to dissolve the excess amount of dithizone, different values has been pointed out in the literature [36,37]. In this investigation, an ammonia solution with the concentration of 2.5% was employed to assure dissolving all the excess amount of dithizone. The optimum volume of the ammonia solution was also investigated and it was found that the volume between 30 and 50 ml was suitable to dissolve the residual reagent without any troublesome on the extraction efficiency. In these experiments, aliquots of 50 ml were used to ascertain the dissolution of the excess amount of dithizone.

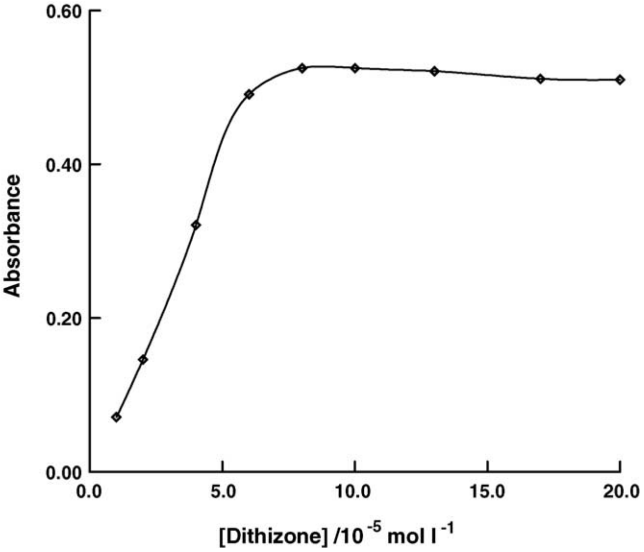

Fig. 1. Effect of dithizone concentration on the determination of Hg(II) by the proposed method. The pH of the solution was adjusted to 5, $C_{\mathrm{Ferroin}}=3.12 \times 10^{-5}$ and $C_{\mathrm{Hg}} = 4.5 \times 10^{-8}$ mol l^{-1} in all of the examinations.

Table 1
Tolerance limits for diverse ions in 8×10^{-8} mol l^{-1} Hg(II) in a 500 ml solution

Mole ratio of interfering ion to Hg(II)	Ions
10000	Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cd^{2+} [a], Co^{2+}, Cu^{2+}[a], Fe^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}[a], Zn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}[a], F^-, Cl^-, Br^-, SCN^-, ClO_4^-, CH_3COO^-, CO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$
2500	Pb^{2+}, Cu^{2+}
500	Fe^{3+}
100	Ag^+, Cd^{2+}

[a] Tolerated after masking with EDTA in which 5 ml of 0.1 M solution was added to the solution before the flotation process.

3.3. Conformity with Beer's law and figures of merit

Under the optimum conditions, a linear calibration curve was constructed for Hg(II) determination over the range of 8.0×10^{-9} to 1.6×10^{-7} mol l^{-1}. The correlation coefficient (R^2) was 0.9969, showing an acceptable linearity of the calibration curve. The apparent molar absorptivity at 490 nm was 6.53×10^6 l mol^{-1} cm^{-1} for a 500 ml aliquot of the extracted aqueous phase. The R.S.D. obtained ($n = 5$) for 8.0×10^{-8} mol l^{-1} of Hg(II) was 3.7% and the detection limit, defined as the sample concentration giving a signal equal to the blank average signal (7 blank) plus three times the standard deviation of the blanks, was found to be 5.0×10^{-10} mol l^{-1}.

3.4. Effect of foreign ions

Possible interference from various ions may be found in the complex matrixes and examined by introducing them into aliquots of Hg(II) solutions with the concentration of 8×10^{-8} mol l^{-1}. The tolerance limit was fixed as the maximum amount of an ion causing an error not greater than 5% in the absorbance of the extract. The results are given in Table 1. It was observed that almost all of the cations and anions are tolerated at high ion/Hg(II) ratio except for Ag^+, Cd^{2+} and Fe^{3+} which exhibit proportionally lower tolerated limits. The lower tolerated limit of Ag^+ may be due to its nearly similar behavior which is exhibited in treatment with the proposed method. The interference of Cd^{2+} is attributed to form a more stable complex with phen as $Cd(phen)_3{}^{2+}$ and produces an ion-associate with iodide. This interfering ion-associate can be floated similarly at the critical concentrations and more. During the extraction of mercury content, it can also be extracted with dithizone in the same manner [38]. It is clear that moderately low tolerance limit of Fe^{3+} is attributed to the oxidation of the iodide ion, so that the flotation process could not be carried out accurately. The tolerance limit of Cd^{2+} and Fe^{3+} were sufficiently enhanced by the addition of 0.01 mol l^{-1} EDTA as a masking agent, but Ag^+ could be neither masked nor separated with none of the conventional agents. Fortunately, the concentration of Ag(I) is very low in usual real sample and Ag^+ is not a serious interferent on the determination of Hg(II) in practical analysis of the real samples [39].

3.5. Application to real samples

The proposed method was applied for the determination of Hg(II) in several water samples including a tap water, a synthetic laboratory seawater and a human hair sample. The synthetic seawater composition was prepared adapting to the literature procedure [40]. Along with the samples, several known amounts of Hg(II) were spiked to examine the reliability of the method. In treatment with the first two samples, aliquots of 500 ml were directly employed and the last, a known weight of 500 mg of hair was initially digested [41], and then the prepared solution was subjected to the proposed method. The recovery of the spiked amounts as shown in Table 2 was in the range of 96.2–102.1% which demonstrates that the proposed method exhibits a good reliability. Since the concentration of Cl^- is essentially very high in seawater, to eliminate its interference in treatment with the flotation step, the iodide concentration was increased up to five times of the normal case. The slopes of the calibration graphs prepared for the water samples were found almost identical with that of the standard addition plot. Hence, the standard curve method with a R.S.D. of 2.52% was used in the determination of various samples.

The validity of the proposed method was checked by comparing the data obtained from the sample analysis with those

Table 2
Analytical data of mercury determination in 500 ml of a tap water, the prepared synthetic seawater and a human hair sample by the proposed and CV-AAS methods

Samples	Spiked (μg)	Measured (μg)[a]			
		This method	Recovery (%)	CV-AAS method	Recovery (%)
Tap water	8.00	8.16 (±0.10)	102.1	8.34 (±0.12)	104.2
	4.00	3.91 (±0.13)	97.8	3.87 (±0.17)	96.7
Synthetic seawater	8.00	7.78 (±0.13)	97.2	8.46 (±0.19)	105.7
	4.00	3.91 (±0.15)	97.9	4.12 (±0.21)	103.0
Human hair	–	4.83 (±0.17)	–	4.56 (±0.13)	–
	4.00	8.68 (±0.13)	96.2	8.72 (±0.17)	104.0

[a] The results are reported as the average values from five samples measurements.

obtained by a well-known method, namely CV-AAS. In these experiments, aliquots of 100 ml of the above samples were examined utilizing $SnCl_2$ as the reducing agent [42]. The results of various sample analyses are listed in Table 2. As it is shown, there are no significant differences between the concentration measurements of Hg(II) by the proposed method and those obtained by CV-AAS method, so that they are in agreement with each other, according to paired *t*-test in 95% confidence level ($t_{crit} = 2.57$ and $t_{exp} = 0.92$). These results demonstrated the applicability of the proposed method to determine extremely low concentration of Hg(II) in various type of the environmental water samples.

4. Conclusion

The developed method offers a good sensitivity and selectivity for the determination of Hg(II) in the range of 1.6–32 $\mu g\, l^{-1}$ in various environmental samples. The important feasibility of the method is its simplicity in treatment with the aqueous samples. Results were found not significantly different from CV-AAS and had less standard deviation in this proposed method than in CV-AAS technique. In comparison with the conventionally dithizone extraction method, the detection limit, sensitivity and selectivity are enhanced considerably due to benefit a high preconcentration factor (100) utilizing the flotation process. The recovery yield and R.S.D. of the measured data denoted that the proposed method can be satisfactorily applied to the determination of trace Hg(II) in real samples.

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